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SYNTHESIS OF TRIPTANE AND RELATED WORK AT THE AZERBAYDZHAN ACADEMY OF SCIENCES

In regard to work on the synthesis of triptane carried out in the USSR and the properties of this high-octane motor fuel component, the following information is contained in two communications published in Priroda and a paper in Neftyanoe Khozyaystvo by V. I. Isagulyants. Numbers in brackets refer to the appended sources.

The most advantageous method for synthesizing triptane is considered to be the procedure discovered by the Khar'kov professor, A. P. El'tekov, in 1873 (Zhur. Russ. Fiz.-Khim. Obsh. Vol X, p 86, 1878; Vol XIV, p 355, 1882). He found that upon heating trimethylene with methyl iodide and lead oxide for 7-8 hours at 210-215 degrees centigrade a mixture of hydrocarbons is obtained which consists to the extent of one third of the total yield of tetramethylethylene and assymetric methyl tert-butyl ethylene

$$CH_2 = C (CH_3) / C(CH_3)_3 / 7$$

The latter can be easily hydrogenated to triptane in the presence of nickel. Moldavskiy, T. Nizovkina, and V. Zharov (Zhur. Obshch. Khim. Vol XVI, p 427, 1946) have shown that lead oxide can be replaced with magnesium oxide, and that the cheaper methyl chloride can be used instead of methyl iodide. The reaction scheme is as follows:

1)
$$(CH_3)_2 C = CH - CH_3 \xrightarrow{+CH_3C1} (CH_3)_2 CC1 = CH(CH_3)_2$$

$$-\text{HCl}$$
 $(\text{CH}_3)_2$ $c = c(\text{CH}_3)_2$ $c\text{H}_2 = c(\text{CH}_3) - c\text{H}(\text{CH}_3)_2$

2)
$$(CH_3)_2 C = C(CH_3)_2 \xrightarrow{+CH_3C1} (CH_3)_2 CC1 - C(CH_3)_3 \rightarrow$$

 $CH_2 = C(CH_3) - C(CH_3)_3$

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The yield of the last hydrocarbon, which may be called triptane, comprises 15% with reference to the trimethylethylene. For purposes of comparison, it ought to be mentioned that the last reaction has been applied in the USA, except that magnesium oxide was replaced by calcium oxide (Verte Miller and W. Lovell, Ind and Eng Chem, 1948, p 1138).

V. I. Isagulyants, whose exact affiliation is not known, but who has published some work in Izv. Armyan. Filiala AN SSR (News of the Armenian Affiliate of the Academy of Sciences of the USSR), gives a general review of developments pertaining to the synthesis of triptane /3/2. He describes the method of El'tekov which had been improved by Moldavskiy et al, as indicated above, and compares this method with the catalytic demethylation of isocotane according to V. Hensel and V. N. Ipat'ev (Ind Eng Chem, Vol XXXIX, p 853, 1947) and the synthesis of triptane by the alkylation of isobutane with propylene in the presence of alkyl halides according to O'Kelly and Sachanen. He considers Ipat'ev's method feasible under certain conditions, in view of the high value of triptane, but regerds the yield obtained in Sachanen's synthesis as too low (the yield comprises 5-6% by weight with reference to the propylene). However, Isagulyants points out that the latter method permits production of triptane without the use of a heterogenous catalyst.

A. V. Kozhevnikov regards the statement, that the use of triptane in combination with tetraethyl lead augments the power of the engine by a factory of four, while one quarter of the quantity of triptane is required as compared with iso-octane (cf Zal'kind, Priroda, Vol XXXVIII, No 1, p 63, Jan 1949), as an exaggeration. $\begin{bmatrix} 1 \\ 1 \end{bmatrix}$

According to Isagulyants $\int 3_7$, the properties of triptane are follows:

Boiling point

80.8° c

Melting point

minus 25° C

20 n

Г

1.3894

ago

0.6901

Octane number of triptane when

admixed to other fuel

112.5

Higher and effective degree of

compression (NPSS)

14.5

In reviewing USSR work on high-octane components of gasoline and in related fields of hydrocarbon chemistry, the following information compiled from recent publications may be considered to advantage.

The review of scientific research at the Azerbaydzhan Academy of Sciences in 1948 (Vestnik Akademii Nauk, No 1, 1949) does not give any information on the synthesis of triptane which is not covered in 00-W-332/50. /Note: As far as can be judged from the Russian text in question, the product referred to in paragraph 4, p 2, 00-W-332/50 is not triptane, but another product the name and composition of which have not been disclosed in the Russian text. In view of the fact that the initial research on which the catalytic process in question is based has been definitely credited to N. D. Zelinskiy, it may be pertinent to outline the work done by Zelinskiy in the field of petroleum chemistry.

As stated by S. V. Kaftanov in "Stalin Prize Laureates in Chemistry in the Decade Since the Founding of the Prize", / 4/7, Zelinskiy has worked on the hydrogenation and dehydrogenation of hydrocarbons, concentrating on cyclication

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and aromatization of open chains. He has also worked on the synthesis of oxygen-containing compounds (alcohols, aldehydes, ketones, and other derivatives) from petroleum raw materials. His work on the catalytic cracking of heavy petroleum components for the production of motor fuel and on the synthesis of valuable aromatic compounds has been of great industrial significance.

On the basis of the information available at present, it is not known whether a general aviation fuel and lubricants development program is being carried out at the petroleum research section of the Azerbaydzhan Academy of Sciences. In view of the fact that the Azerbaydzhan Academy, which is known to have a division of chemical sciences and petroleum, is a part of the Transcaucasian Affiliate of the Academy of Sciences USSR, and that it is located in one of the principal centers of petroleum production, a rather close connection with the Institute of Petroleum of the Academy of Sciences USSR may be assumed.

It may be of interest to note in this connection that Prof A. D. Petrov, head of the Laboratory of Pyrogenic Processes, Academy of Sciences USSR, is referred to as a consultant of the Azerbaydzhan Affiliate of the Academy of Sciences USSR. A general review of Prof Petrov's work, which includes investigations in the field of synthetic lubricating oils, is given in 00-W-4020/49 (cf Vestnik Akademii Nauk SSSR, Vol, XVI, No 2, 1946). From the point of view of the synthesis of isoparaffins, Petrov's work on the isomerization of olefins seems to be relevant. The double bond of olefins can be displaced under the conditions of heterogenous catalysis, according to N. D. Zelinskiy, R. Ya. Levina, and A. D. Petrov.

A. D. Petrov and V. I. Shchukin (Zhur. Obshch. Khimii, Vol IX, 506, 1939; Vol XI, p 1092, 1941) have shown that at high temperatures and pressures heptene-1 and octene-1 are transformed into methylethylethylene and dimethylbutylethylene respectively. Furthermore, the isomerization of butylene into isobutylene was carried out in the presence of clay and floridin (A. V. Frost, Zhur. Obshch. Khimii, Vol VII, 122, 1937) and the identical reaction also takes place over aluminium--silicate catalysts according to G. I. Maslyanskiy and M. V. Veltisova, Zhur. Obshch. Khimii, Vol. XVI, p 2134, 1946 / 2 //. A. D. Petrov successfully converted normal hexene into the maximally branched 2, 3-dimethylbutene / 47.

A. D. Petrov collaborating with A. I. Antsus (Symposium, Soviet Chemistry During 25 Years, 1944, A. D. Petrov, pp 211 and 215) also investigated the aluminium chloride induced polymerization of ethylene, pseudotutylene, or butylene fraction of pyrolysis gases. Acetylene obtained from methane and mixed with hydrogen can be converted into isobutylene under hydrogenation by the so-called cross-polymerization type of reaction and into mixtures of other olefinic hydrocarbons by linear polymerization \(\subseteq 2 \). According to S. V. Kaftanov, Petrov's process for the preparation of isobutylene from acetylene will be utilized industrially in the near future in connection with the trend towards greater use of power equipment. The calcium carbide industry will be stimulated by this development.

SCURCES

- Prof Yu. S. Zal'kind, Priroda, (Nature) Vol XXXVIII, No 1, p 63, Jan 1949; A. V. Kozhevnikov, Priroda, Vol XXXIX, No 2, Feb 1950, p 24.
- S. N. Danilov, Trends of Development of USSR Chemistry During the Period of Stalin's Five-Year Plans (Section on Petroleum and Hydrocarbon Research), Zhurnal Obshchey Khimii (Journal of General Chemistry), Vol XX, No 1, 1950, pp 13-14.

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- 3. V. I. Isagulyants, The Synthesis of Triptane, Neftyanoe Khozyaystvo, Vol XXVI, To 11, Nov 1948, pp 49-56.
- 4. S. V. Kaftanov, Uspekhi Khimii, Vol XIX, Jan Feb 1949.

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